

## Noble Gas Permeability of Polymer Films and Coatings

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### Synopsis

Permeabilities of noble gases, particularly argon, krypton, and xenon, were measured through a number of polymer films and coatings. Extrapolation of the log of the permeation coefficient versus the square of the gas molecular diameter was used to estimate radon permeability. An equation has been developed that can predict permeability to these noble gases as a function of the base polymer structure of the coating.

### INTRODUCTION

In connection with work for the U.S. Bureau of Mines,<sup>1</sup> we measured permeability of radon through prospective coatings for uranium mines. Coatings of sufficiently low permeability will retard the passage of radon long enough so that it will decompose naturally into the particulate daughter products, which will be permanently trapped in the coating, thereby reducing the exposure to radiation of uranium miners. Direct measurement of radon permeability is difficult, costly, and slow. To facilitate selection of coatings, we wanted to estimate radon permeability from permeability of nonradioactive noble gases, and to predict radon permeability from the base polymer structure of the coating.

In this work, we found a straight-line extrapolation of the log of the permeation coefficients of argon, krypton, and xenon through a number of polymer films versus the square of the gas molecular diameter. From this extrapolation, we can estimate the radon permeation coefficient, as confirmed by two direct measurements.

It would be helpful in selecting sealants as radon barriers if we could predict radon permeation as a function of the structure of the sealant base polymer. Many chemical, morphologic, and structural properties of the polymer can affect its permeability. After examining several of these properties, we found a correlation between noble gas permeation of a number of polymers and the oxygen Permachor equation developed by Salame.<sup>2</sup> Because the oxygen Permachor is related to the structure of the polymer, we were able to develop an equation that related noble gas permeation coefficients to polymer structure. The equation can be used to estimate the permeation of radon, as well as other noble gases, through polymers.

## EXPERIMENTAL

### Selection and Preparation of Films and Coatings

Commercial extruded- or cast-polymer films of known composition 0.01 to 0.13 mm (0.5 to 5 mils) in thickness were selected for the permeability study. Over this thickness range, there did not appear to be a thickness effect. Most of the coatings were prepared by drawing a solution or latex with a doctor blade onto a substrate of known permeability such as Surlyn A. This polyethylene ionomer had high permeability and was wetted better than conventional polyethylene. The coatings were allowed to dry thoroughly at room temperature and were conditioned for several days at about 50% relative humidity. The thickness of the films or coatings was measured with an electronic micrometer, and averaged values were rounded off to the nearest 0.025 mm (0.0001 in.).

### Determination of Permeation Coefficients

To determine the permeation coefficients of the noble gases, we relied on two techniques: a sensitive method using a mass spectrometer as a gas detector and a Dow film permeability cell. We also determined radon permeation directly, using equipment built especially for that purpose.

In the mass spectrometer method, a thin film (up to 380  $\mu\text{m}$ ) of sealant forms a membrane in a specially designed permeation cell. The cell is evacuated on both sides of the membrane until the gas background is negligible. The test gas is then applied at a known pressure on one side of the membrane. Permeation of the test gas through the membrane is compared to a known, constant flow of the same gas. For this information, we calculate the permeation rate. Knowing the pressure differential across the membrane and the membrane's thickness and area, we then determine the permeation coefficient.

This method is efficient and accurate. Interfering membrane outgassing and desorption gases can be distinguished from the test gas, and pinholes in, or leaks around, the membrane are readily recognized. However, the technique is time consuming for film of low permeability or for higher molecular weight gases such as krypton or xenon.

The Dow film permeability cell<sup>3</sup> has the advantage of greater speed because it uses larger films and has a greater pressure differential. A film is clamped with an O-ring against a permeable surface. There is a vacuum below the surface, and the test gas is introduced at a known pressure above the surface. The rate of gas permeation is measured by the rate of change on a manometer below the sample.

Permeation measurements are more difficult for radon than for the other noble gases. Because of its large gas molecule and slow diffusion rate, the permeation rate of radon is slow. Yet its short half-life means that radon deposits its daughter products in the measuring apparatus. Nevertheless, for comparison, we measured radon permeation through polyethylene and polycarbonate films, using apparatus made especially for the purpose from glass tubing. The apparatus was divided into two chambers by a thin film, and radon from a radium solution was admitted to one side. The gas that permeated the film to the other side was measured by alpha counting.

## RESULTS AND DISCUSSION

The permeation coefficients of some commercial films are listed in Table I, and the permeation coefficients of some supported coatings are listed in Table II. Some of these data are plotted in Figures 1 and 2 as the logs of the permeation coefficients versus the square of the diameter of the permeant gas. Values for the diameter of the noble gases, except for radon, were taken from reference 4. The value for radon is only approximate and was calculated by Klaus Ernst from viscosity measurements. In general, good straight-line fits were obtained for argon, krypton, and xenon permeation coefficients, although the helium and neon permeation coefficients did not usually fit well with the other data. Direct measurements of the radon permeation coefficients were made only through polyethylene and polycarbonate films. As may be seen from Figure 1, these values agreed well with values that would be predicted by extrapolation of the argon, krypton, and xenon values.

The permeation coefficients for noble gases through polyethylene and Surlyn A increase with increasing gas molecular weight and diameter. Similar effects have been reported for neon and argon permeation through ethylene-propylene copolymers, styrene-butadiene copolymers, and a *cis*-polybutadiene;<sup>5</sup> for neon, argon, krypton, and xenon through natural rubber;<sup>6</sup> and for neon, argon, krypton, and xenon through silicone rubber.<sup>7</sup> In polymers of higher cohesive energy density, however, the permeation coefficients of the noble gases decrease with increasing gas molecular weight and diameter, as shown by our data and the data of Meares.<sup>8,9</sup>

TABLE I  
Permeation Coefficients of Commercial Films

Film	Gas	Permeation coefficients	
		cm <sup>3</sup> (S.T.P.)·cm/ sec·cm <sup>2</sup> ·cm Hg	nm <sup>2</sup> /Pa·sec
Polyethylene	He	$6.7 \times 10^{-10}$	50
	Ar	$3.4 \times 10^{-10}$	25
	Kr	$4.5 \times 10^{-10}$	34
	Xe	$8 \times 10^{-10}$	60
	Rn	$1.5 \times 10^{-9}$	113
Surlyn A (polyethylene ionomer)	Ne	$2.0 \times 10^{-10}$	15
	Ar	$1.3 \times 10^{-10}$	9.8
	Kr	$1.5 \times 10^{-10}$	11
	Xe	$1.9 \times 10^{-10}$	14
Polycarbonate	He	$1.5 \times 10^{-9}$	113
	Ar	$5.5 \times 10^{-11}$	4.1
	Kr	$5 \times 10^{-11}$	3.8
	Xe	$2 \times 10^{-11}$	1.5
	Rn	$1.8 \times 10^{-11}$	1.4
Poly(vinyl chloride), unplasticized	He	$4.0 \times 10^{-10}$	30
	Ar	$7.0 \times 10^{-12}$	0.53
	Kr	$3.5 \times 10^{-12}$	0.26
	Xe	$4 \times 10^{-11}$	0.03
Phenoxy	Ne	$2.5 \times 10^{-11}$	1.9
	Ar	$2.6 \times 10^{-12}$	0.20
	Kr	$1.1 \times 10^{-12}$	0.08
	Xe	$2.1 \times 10^{-13}$	0.016

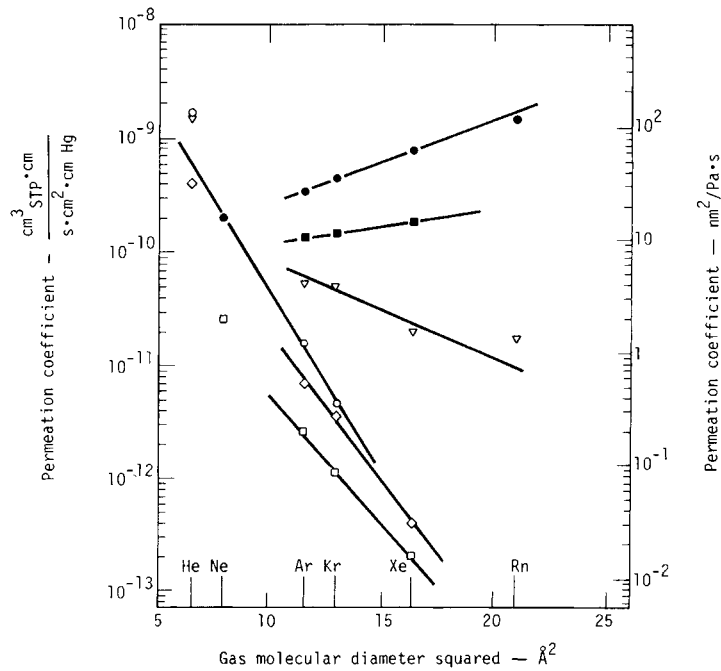


Fig. 1. Permeation coefficients of films vs. square of the gas molecular diameter: (○) poly(vinyl acetate) (Meares); (●) polyethylene; (■) Surlyn A (ionomer); (▽) polycarbonate; (◇) poly(vinyl chloride), unplasticized; (□) phenoxy.

TABLE II  
Permeation Coefficients of Supported Coatings<sup>a</sup>

Description	Permeation coefficients, cm <sup>3</sup> (S.T.P.)·cm/sec·cm <sup>2</sup> ·cm Hg (nm <sup>2</sup> /Pa·sec)		
	Ar	Kr	Xe
Poly(methyl acrylate), low viscosity	3.9 × 10 <sup>-11</sup> (2.9)	N.D.	N.D.
Vinyl chloride copolymer, latex	6.0 × 10 <sup>-12</sup> (0.45)	N.D.	N.D.
Vinylidene chloride copolymer, latex	4.4 × 10 <sup>-13</sup> (0.033)	2.2 × 10 <sup>-13</sup> (0.017)	8.9 × 10 <sup>-14</sup> (0.0067)
Epoxy, pigmented, from water dispersion	7.3 × 10 <sup>-12</sup> (0.55)	6.8 × 10 <sup>-12</sup> (0.51)	5.0 × 10 <sup>-12</sup> (0.38)
Epoxy, not pigmented, from water dispersion	1.1 × 10 <sup>-11</sup> (0.83)	7.7 × 10 <sup>-12</sup> (0.58)	3.5 × 10 <sup>-12</sup> (0.26)
Poly(vinyl acetate), plasticized, latex	2.4 × 10 <sup>-11</sup> (1.8)	1.1 × 10 <sup>-11</sup> (0.83)	1.9 × 10 <sup>-12</sup> (0.14)
Styrenated polyester, pigmented	1.7 × 10 <sup>-10</sup> (13)	N.D.	N.D.

<sup>a</sup> N.D. = Not determined.

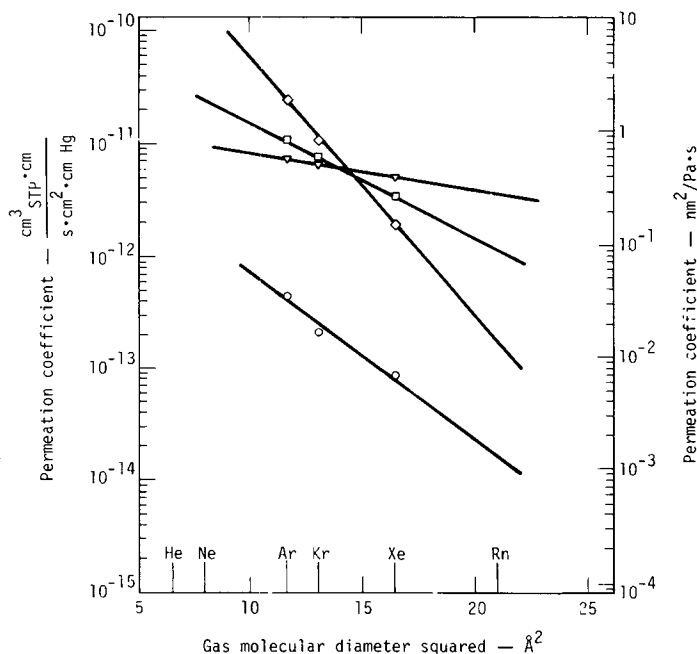


Fig. 2. Permeation coefficients of coatings vs. square of the gas molecular diameter: ( $\square$ ) epoxy, not pigmented; ( $\diamond$ ) poly(vinyl acetate), plasticized; ( $\nabla$ ) epoxy, pigmented; ( $\circ$ ) vinylidene chloride copolymer latex.

### Correlation of Permeability with Polymer Structure

In selection of coatings as radon barriers, it would be desirable to predict the radon permeation coefficient based on the structure of the base polymer used in the coating. For this reason, we made some studies of possible relationships. Many chemical, morphologic, and structural properties of the polymer can affect the permeability of a polymer.<sup>10-13</sup> These include chemical properties such as cohesive energy density (CED) and hydrogen bonding, morphologic properties such as crystallinity and orientation, and the effect of structural groups in the polymer chain. It was quickly apparent that CED alone would not correlate with permeability, but we did find a reasonable correlation of the product of CED and polymer density with argon permeability, as shown in Figure 3. This correlation did not appear to hold with the higher molecular weight noble gases. We then tried linear regression analysis with a number of polymer properties including CED, density, refractive index, gas molecular diameter ( $d$ ), and  $d^2$ . The results were not particularly promising. We observed, however, that there was a correlation of the argon permeability of a number of polymers with the oxygen Permachor as developed by Salame<sup>2</sup> (see Fig. 4). This relationship was later extended to the other noble gases. Although Salame developed the Permachor equation empirically, he showed that there was a definite relationship to the classical relationship between permeability, diffusion, solubility, and temperature:

$$P = DS = (D_0S_0) \exp -[(E_d + \Delta H)/RT]$$

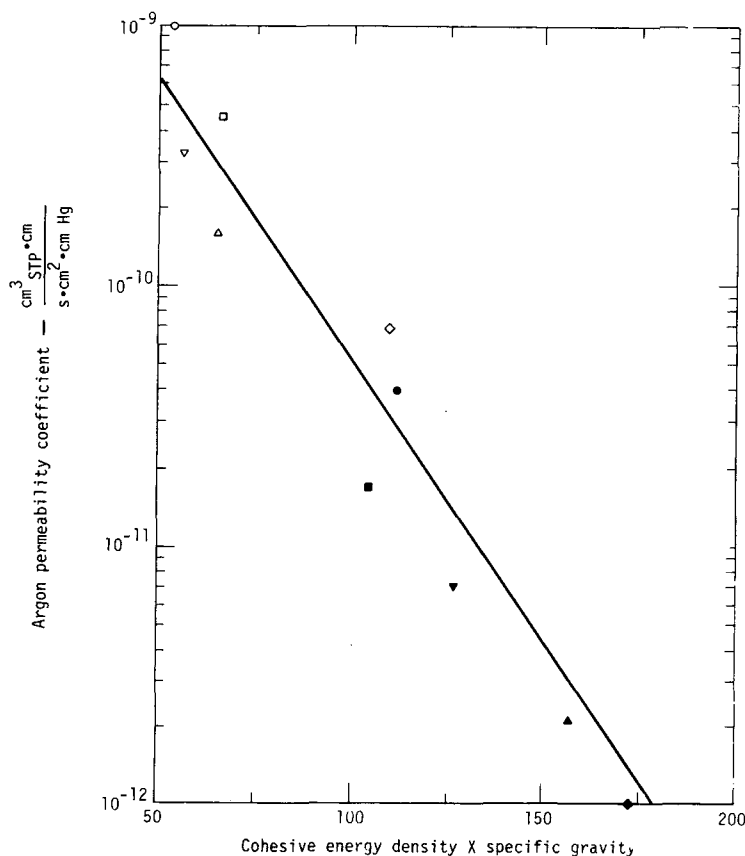


Fig. 3. Argon permeability coefficient vs. cohesive energy density times specific gravity: (O) ethylene-propylene rubber; (□) styrene-butadiene rubber; (▽) polyethylene; (Δ) Surlyn A; (◇) polycarbonate; (●) poly(methyl acrylate); (■) poly(vinyl acetate); (▼) poly(vinyl chloride); (▲) phenoxy; (◆) Saran XD-4624.

where  $P$  is the permeability coefficient,  $D$  is the diffusion coefficient,  $S$  is the solubility coefficient,  $E_d$  is the energy of diffusion, and  $\Delta H$  is the heat of solution of the gas in the polymer; both  $D_0$  and  $S_0$  are preexponential factors from the Arrhenius equations,  $R$  is the gas constant, and  $T$  is absolute temperature.

Salame's Permachor equation for the oxygen permeability of polymers at 25°C is  $P = (6.1 \times 10^{-9}) \exp -0.115I$ , where  $I$  is the oxygen Permachor. The Permachor equation can also be written

$$P = \exp -0.115 I \cdot \exp[-(11200/RT)]$$

which can be written in the form

$$P = \exp (A + BI) \text{ or } \ln P = A + BI$$

where  $A$  can be related to  $(E_d + \Delta H)/RT$ , and the coefficient  $B$  is determined by fitting experimental data.

We have studied the permeability of the noble gases, especially argon, krypton, and xenon, and have found that a relationship exists between the factors  $A$  and  $B$  and the square of the gas molecular diameters. Apparently, it is possible to

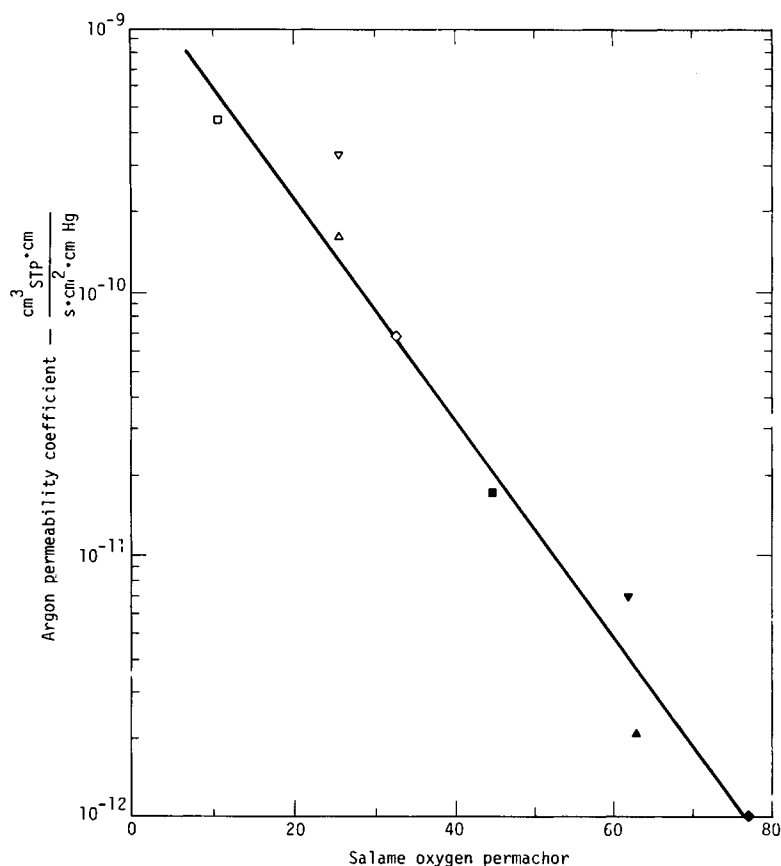


Fig. 4. Argon permeability coefficient vs. Salame oxygen Permachor: (□) styrene-butadiene rubber; (▽) polyethylene; (Δ) Surlyn A; (◇) polycarbonate; (■) poly(vinyl acetate); (▼) poly(vinyl chloride); (▲) phenoxy; (◊) Saran XD-4624.

extrapolate to random permeability through the determination of these relationships.

Because the data were limited to argon, krypton, and xenon, a linear relationship was used. A least-squares fit was made of the oxygen Permachor to the permeability data we had determined for phenoxy, poly(vinyl chloride), polycarbonate, polyethylene ionomer (Surlyn A), and Meares<sup>8,9</sup> data for poly(vinyl acetate). The coefficients  $A$  and  $B$  of the gases argon, krypton, and xenon thus obtained appeared to be linearly related to the  $d^2$  of the gases. The least-squares fit of this relationship resulted in the final equation

$$\ln(10^2 P) = (4.2354 + 0.4166d^2) + (0.088 - 0.0155d^2)I$$

where  $P$  = permeability coefficient, in nm<sup>2</sup>/Pa·sec;  $d^2$  = gas diameter squared, in Å<sup>2</sup>; and  $I$  = Salame's oxygen Permachor. (Salame used the symbol  $\pi$ (pi) for Permachor. We used  $I$  to avoid confusion with the conventional use of  $\pi$ .) Calculated values, using this equation, are shown in Table III along with our experimentally determined values for a number of polymers and coatings. The fit is quite good in most cases, but is rather poor for polyethylene. Because the Permachor is related to the structure of the polymer, this equation establishes

TABLE III  
Permeability Coefficients of Polymers Calculated from Permachor

Material	Perma- chor <i>I</i>		Permeability, nm <sup>2</sup> Pa-sec				
			Ne	Ar	Kr	Xe	Rn
Phenoxy film	63	Exp.	1.9	0.20	0.08	0.016	—
		Calc.	2.0	0.27	0.12	0.02	0.0015
Poly(vinyl chloride) film, unplasticized	62	Exp.	—	0.53	0.26	0.03	—
		Calc.	2.1	0.29	0.14	0.02	0.0019
Polycarbonate film	33	Exp.	—	4.1	3.8	1.5	1.4
		Calc.	5.9	4.2	3.7	2.7	1.7
Surlyn A film	26	Exp.	15	9.8	11	14	—
		Calc.	7.6	7.8	8.1	8.5	9.1
Poly(vinyl acetate) (data of Meares)	45	Exp.	15	1.1	0.36	—	—
		Calc.	3.8	1.4	0.94	0.36	0.10
Epoxy, pigmented coating <sup>a</sup>	50	Exp.	—	0.55	0.51	0.38	—
		Calc.	3.2	0.88	0.53	0.16	0.03
Epoxy, unpigmented coating <sup>b</sup>	55	Exp.	3.4	0.83	0.58	0.26	—
		Calc.	2.7	0.56	0.30	0.07	0.001
Poly(vinyl acetate), <sup>c</sup> plasticized coating	43	Exp.	—	1.8	0.83	0.14	—
		Calc.	4.1	1.7	1.2	0.50	0.16
Polyethylene film	26	Exp.	—	25	34	60	113
		Calc.	7	7.8	8.1	8.5	9.1
$d^2, \text{\AA}^2$			8.0	11.6	13	16.4	20.9

<sup>a</sup>Permachor estimated and arbitrarily lowered for pigment content.

<sup>b</sup>Permachor estimated.

<sup>c</sup>Permachor arbitrarily lowered for plasticizer content.

a definite relationship to polymer structure and can be used to estimate the permeability of radon as well as the other noble gases through polymers.

There are relatively few permeability data in the literature for the noble gases since the major interest is in nitrogen, oxygen, carbon dioxide, and water as they may affect packaging of foods, etc. However, Burgess et al.<sup>14</sup> have measured the permeability of poly(methyl acrylate) to argon and krypton and reported values equivalent to 1.3 and 0.75 nm<sup>2</sup>/Pa-sec at 20°C. The oxygen Permachor of poly(methyl acrylate) calculated from Salame's segmental values is 51. Using this value in the above equation, we calculate values for argon and krypton of 0.8 and 0.48 nm<sup>2</sup>/Pa-sec, which agree to better than a factor of 2 with the experimentally determined values.

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